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(54) Title: OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

(57) Abstract

This invention pertains to a catalyst containing a monolith impregnated with a Cr containing compound. In addition, the invention pertains to the production of olefins by the reacting hydrocarbons and an oxygen containing gas in the presence of a catalyst containing a chromium compound, a copper containing compound, a manganese containing compound and a combination thereof supported on a monolith.

OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

CROSS REFERENCE TO RELATED APPLICATIONS

5   This application is claims benefit to provisional application 60/117,095 filed January 25, 1999, which is incorporated by reference in its entirety for all useful purposes.

FIELD OF THE INVENTION

10   This invention pertains to the production of olefins by the oxidative dehydrogenation or cracking of saturated hydrocarbons over a catalyst containing chromium and/or chromium oxide. High yields of olefins can be obtained over structured catalysts with very short contact times and no catalyst deactivation.

BACKGROUND OF INVENTION

15   Currently, olefins are used as important chemical intermediates for a large number of industrial processes and consumer products. These light olefins such as ethylene, propylene, and butenes are usually produced by the steam pyrolysis process [Pyrolysis: Theory and Industrial Practice; Albright, L. F. et al, Eds.; Academic Press: New York, 1983]. The two major limitations of the current steam pyrolysis process are the high gas temperatures (800-900°C) required and the deposition of coke on the walls of the reactor tube that require the periodic shut-down of the process for decoking. To overcome these limitations, there has been much recent interest in trying to find a catalytic alternative to the current industrial steam cracking process.

25   Many researchers have investigated the catalytic dehydrogenation of light alkanes as a route to obtaining alkenes for polymerization and other organic synthesis. This approach does not cofeed an oxidant. Much of this research has focused on

E.. *J. Catal.* **1993**, *142*, 166-171; Hoang, M.; Hughes, A. E. et al, *J. Catal.* **1997**, *171*, 313-319; Hoang, M. et al, *React. Kinet. Catal. Lett.* **1997**, *61*, 21-26; Zaki, M. I. et al, *Appl. Catal.* **1986**, *21*, 359-377]. Thus, the catalytic properties of supported chromium catalysts are strongly affected by the acidity/basicity of the oxide support. However,

5   there is significant disagreement over the exact oxidation state of the active Cr surface species. Recent research has also examined the use of supported chromium oxide catalysts for the catalytic dehydrogenation of hydrocarbons [De Rossi, S. et al, *Appl. Catal. A: General* **1992**, *81*, 113-132; De Rossi, S. et al, *Appl. Catal. A: General* **1993**, *106*, 125-141; De Rossi, S. et al, *J. Catal.* **1994**, *148*, 36-46; Lugo, H. J. and Lunsford,

10   J. H., *J. Catal.* **1985**, *91*, 155-166; Udomsak, S. and Anthony, R. G., *Ind. Eng. Chem Res.* **1996**, *35*, 47-53].

SUMMARY OF THE INVENTION

This invention describes the production of olefins by catalytic partial oxidation of

15   saturated hydrocarbons on chromium oxide supported on monoliths at very short contact times. This catalyst and process can be significantly less expensive to operate than either a standard packed bed reactor using a selective oxide catalyst at a residence time in excess of 0.1 seconds or the newer short contact time oxidative dehydrogenation process using monolithically supported noble metals. Additionally, this

20   catalyst produces less by-product CO which is advantageous to downstream processes. The monoliths may be composed of any oxide stable at temperature in excess of 900°C including α-Al_2O_3, SiO_2, Mg-stabilized ZrO_2, and Y-stabilized ZrO_2 and may have a honeycomb or foam structure although the foam structure is preferred. The support affects the activity of the chromium oxide catalyst as does the presence of

25   various promoters, including Cu, Mn, Mg, Ni, Fe, their oxides, and combinations

thereof. The preferred promoters are copper and copper oxides. The preferred metal atom ratio of promoter to chromium is between 1:100 and 1:2 and more preferably between 1:15 and 1:5.

To summarize these results, supported chromium oxide has been shown to be an effective catalyst for the oxidative dehydrogenation of ethane. As reported in the literature, the activity of the supported chromium oxide catalyst has been shown to depend upon the ceramic support material [Hoang, M. et al, *J. Catal.* **1997**, *171*, 313-319], the surface area, and the chromium oxide loading (with a lower loading showing a lower activity and shorter lifetime). The high loading chromium oxide catalyst supported on ZrO_2 monolith showed the best overall activity of all the supported chromium oxide catalysts, but could not achieve stable operation at flow rates higher than 5 SLPM. The 9 wt. % Cr_2O_3/ZrO_2 catalyst outperformed the Pt-coated monolith with a higher C_2H_4 selectivity and C_2H_6 conversion, and thus higher C_2H_4 yield. It was also found that the addition of copper to the chromium oxide on ZrO_2 catalyst significantly increased the activity of the catalyst such that stable operation with no signs of deactivation was with GHSV (STP) up to 1×10^6 hr^{-1}. The addition of copper to the Cr_2O_3/ZrO_2 catalyst, however, did not significantly affect the product selectivity or reactant conversions.

DETAILED DESCRIPTION OF INVENTION

Any short contact time reactor can be used. The reactor used here is essentially identical to that previously described for the production of syngas [Hickman, D. A. and Schmidt, L. D., *J. Catal.* **1992**, *136*, 300-308 and references therein] and oxidative dehydrogenation of light alkanes [Flick, D. W. and Huff, M. C., *J. Catal.* **1998**, *178*, 315-327 and references therein; Huff, M. and Schmidt, L. D., *J. Phys. Chem.* **1993**, *97*,

11815-11822 and references therein]. The reactor consists of a quartz tube with an inner diameter of 20 mm. The catalyst is sealed in the tube with high temperature silica-alumina felt which prevents the bypass of gases around the catalyst. To reduce the radiation heat loss in the axial and radial directions and to better approximate adiabatic operation, inert foam monoliths are placed in front and behind the catalyst as heat shields, and the reaction zone is externally insulated.

A ceramic foam monolith with 20-100 pores per linear inch (ppi) is impregnated with a Cr containing precursor such as an aqueous solution of $Cr(NO_3)_3$, and then calcined in air at 600°C for at least four hours. After calcination, the chromium oxide coated monoliths were bright green in color. The chromium oxide can be supported on monoliths made from high temperature (>900°C) stable oxides including α-Al_2O_3, SiO_2, Mg-stabilized ZrO_2, and Y-stabilized ZrO_2. Pt and mixtures of promoters (Cu, Mn, Mg, Ni, Fe, and combinations thereof) were deposited on the monoliths similarly using H_2PtCl_6 or transition metal nitrate salts, respectively, in an aqueous solution. The monoliths used measured 10 mm thick and between 18-20 mm in diameter.

The gas flow for the reactor is controlled by electronic mass flow controllers. The total feed flow rate to the reactor ranged from 0.1 to 12 SLPM which corresponds to approximate contact times of 2-200 milliseconds (GHSV = 1 x 10^5 – 2.2 x 10^6 hr^{-1} at STP) for the monolith catalyst. The reactor operates near atmospheric pressure. The reaction occurs autothermally around 900°C.

While the reaction operates autothermally at steady state, an external heat source is necessary to ignite the reaction. The gas mixture with C_2H_6:O_2:N_2 = 25:15:60) ignites at approximately 350°C over the chromium oxide catalyst at a flow rate of 3 SLPM which is higher than the 220°C preheat needed to ignite that reaction over a Pt coated monolith catalyst. After ignition, the external heat source is removed or

reduced to the desired level of heat addition, the composition is adjusted to the desired value and steady state is established. After each change in feed conditions, the reactor is allowed to achieve steady state (<10 min.) before analysis of the reaction products by the GC.

The feed gas consists of C_2H_6 and O_2 with N_2 as the diluent. The level of dilution ranged from <1 to about 80%. The N_2 was used as an internal GC calibration standard. Additional trials have been completed using alternative diluents: N_2, He, Ar, CO_2, H_2O and mixtures thereof. Some experiments were conducted with the feed composition within the flammability limits. In these instances, it is important to realize that this is a flow system with linear velocities in excess of the flame speed such that homogeneous ignition is impossible [Bolk, J. W. et al, Chem. Eng. Sci. 1996, 51].

The reaction temperature was measured by a type K (chromel/alumel) thermocouple inserted from the rear of the reactor and placed at the center of the reactor tube between the catalyst and the rear radiation heat shield. The temperature measured at the back of the catalyst, the reaction temperature, is a good measure of both the product gas phase temperature and the surface temperature of the rear face of the catalyst, since the gas phase and surface temperatures are approaching equilibrium at the catalyst exit.

In some experiments, the feed gas to the reactor contained C_2H_6, O_2, and H_2 with a small amount of N_2 for use as an internal calibration standard. The level of H_2 in the feed ranged from 0 to 50% which corresponds to H_2/O_2 ratios ranging from 0 to 3.0. The amount of N_2 in the feed was always less than 1%. The process could recycle the H_2 and not require a net import of H_2 to the system.

The catalyst can contain substantially no Pt. Substantially no Pt means less than 0.1% Pt by weight, preferably less than 0.01 % Pt by weight.

Table 7: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 4 wt. % Cr_2O_3/ZrO_2 monolith as a function of flow rate at a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm.

Flowrate (SLPM)	1	2	3
Carbon atom selectivity (%)			
C_2H_4	56.6	51.7	48.2
CO	22.8	23.1	24.7
CO_2	9.8	7.9	7.7
CH_4	7.5	9.8	9.8
C_2H_2	0.01	0.9	6.1
Other	3.3	6.6	3.5
Hydrogen atom selectivity (%)			
H_2	34.7	36.6	42.7
H_2O	24.7	21.8	16.0
Conversion (%)			
C_2H_6	89.5	92.3	93.3
O_2	99.5	99.4	99.7
Temperature (°C)			
Front	1025	1053	367
Rear	840	895	954

Table 8: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 6.7% Cu - 6.7% Cr_2O_3/ZrO_2 monolith as a function of flow rate at a C_2H_6/O_2 ratio of 2.4 with 20% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm.

Flowrate (SLPM)	2	3	4
Carbon atom selectivity (%)			
C_2H_4	71.4	69.9	67.1
CO	7.3	7.3	7.2
CO_2	14.1	11.8	11.3
CH_4	3.6	3.9	3.7
C_2H_2	0.5	0.7	0.4
Other	3.0	6.5	10.2
Hydrogen atom selectivity (%)			
H_2	16.3	17.3	15.9
H_2O	28.4	24.0	23.3
Conversion (%)			
C_2H_6	58.0	64.4	65.0
O_2	99.8	99.7	99.6
Temperature (°C)			
Front	245	146	108
Rear	738	760	756

could not be sustained for even a few minutes. Thus, for the Cr_2O_3/Al_2O_3 catalyst, the reaction can only be sustained inside the flammability range for the C_2H_6, O_2, and N_2 system, and the lifetime decreases the closer the mixture is to the upper flammability boundary. However, in stark contrast to the Cr_2O_3/Al_2O_3 catalyst, the 9 wt. % Cr_2O_3/ZrO_2 monolith sustained steady reaction up to a C_2H_6/O_2 ratio of 1.8 with 50% N_2 dilution for over 2 hours and at a C_2H_6/O_2 ratio of 1.5 with 50% N_2 dilution at 2 SLPM, the Cu modified Cr_2O_3/ZrO_2 monolith catalyst did not show any deactivation for over 7 hours of continuous operation, while all of the previous chromium oxide containing catalyst rapidly extinguished at a C_2H_6/O_2 ratio of 1.5 with 50% N_2 dilution.

The effects of preheat are shown in Tables 9-10 for the 9 wt. % Cr_2O_3/α-Al_2O_3 monolith catalyst at a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution at a flowrate of 2 SLPM. Results are shown as a function of time for nearly adiabatic operation (Table 9) and for

autothermal operation (Table 10) where the reactants have been heated to 250°C before reaching the reaction zone. Preheat results in a catalyst lifetime of ~7 hours before the reaction extinguished. The addition of preheat, however, leads to a slightly lower selectivity to C_2H_4 and a higher selectivity to CO. Preheating the feed also

5   increased the selectivity to CH_4 and C_2H_2 and decreased the selectivity to CO_2. As expected, the C_2H_6 conversion increases with preheat.

The most interesting impact of preheat is shown in the temperature of the catalysts. The front and back temperature of the catalyst without preheat and the front temperature of the catalyst with preheat fall dramatically after approximately 1.5 hours

10   of operation. However, the addition of preheat seems to provide enough energy to keep the reaction ignited with relatively stable front and back temperatures over the catalyst for several hours after the catalyst without preheat extinguished. The 250°C preheat of the feed, however, did not provide enough energy to keep the reaction from eventually extinguishing. There were also slight selectivity changes to C_2H_4, CH_4, and CO that

15   correspond with the rapid drop in the temperature at the front of the catalyst.

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Table 9: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 9 wt. % Cr_2O_3/ α-Al_2O_3 monolith as a function of time at a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm. Data is shown for reactants entering the reactor at room temperature.

Time on stream (hr)	0.0	0.5	1.0	1.5	
Carbon atom selectivity (%)					
C_2H_4	41.8	46.2	46.6	42.8	Extinguished
CO	27.8	25.5	26.6	32.4	after ~1.7 hrs.
CO_2	6.8	8.6	8.2	7.2	
CH_4	11.3	10.1	10.0	11.1	
C_2H_2	8.3	5.8	5.0	3.6	
Other	4.0	3.8	3.6	2.9	
Hydrogen atom selectivity (%)					
H_2	42.1	42.0	43.1	43.3	
H_2O	17.2	17.1	16.4	17.2	
Conversion (%)					
C_2H_6	97.6	95.8	95.1	88.6	
O_2	100	99.8	99.8	99.2	
Temperature (°C)					
Front	390	187	164	56	
Rear	1015	1025	998	870	

Table 10: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 9 wt. % Cr_2O_3/ α-Al_2O_3 monolith as a function of time at a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm. Data is shown for reactants entering the reactor at 250°C temperature. The reaction extinguished between hours 7 and 8.

Time on stream (hr)	0.0	0.5	1.0	1.5	2.0	4.0	6.0	7.0
Carbon atom selectivity (%)								
C_2H_4	36.3	36.6	36.5	39.1	40.5	40.4	41.1	37.0
CO	33.2	34.0	34.6	30.0	29.9	30.7	29.5	37.2
CO_2	5.0	4.7	4.3	3.5	3.3	3.3	2.9	3.5
CH_4	13.2	13.0	13.0	14.0	14.4	14.3	14.4	12.8
C_2H_2	9.1	8.4	7.8	7.9	7.7	7.3	6.6	5.8
Other	3.2	3.3	3.8	5.5	4.2	4.0	5.5	3.7
Hydrogen atom selectivity (%)								
H_2	46.8	47.2	47.6	42.9	42.8	42.9	40.7	50.8
H_2O	14.6	14.4	14.1	14.1	14.4	14.5	15.1	10.8
Conversion (%)								
C_2H_6	98.5	98.3	98.2	98.0	97.9	97.9	97.5	97.8
O_2	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
Temperature (°C)								
Front	1180	1132	1112	670	640	595	580	565
Rear	1000	962	895	870	840	825	818	760

Example 6: The oxidative dehydrogenation of ethane was investigated with different diluents including N_2, Ar, CO_2 and H_2O. The carbon and hydrogen atom selectivities, conversions and temperatures for the oxidative dehydrogenation over a 1.0 wt. % Cu – 9.0 wt. % Cr_2O_3/ZrO_2 catalyst at C_2H_6/O_2 ratios of 1.8 and 2.4 at a total flow rate of 2 SLPM with 20% dilution are shown in Tables 11 and 12. The product selectivities are not significantly affected by changes in the type of diluent. The ethane conversion,

Table 11. Carbon and hydrogen atom selectivity, conversion, and temperature for ethane oxidative dehydrogenation over a 1.0 wt. % Cu – 9.0 wt. % Cr_2O_3/ZrO_2 catalyst at a C_2H_6/O_2 ratio of 1.8 with 20% total dilution at a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Diluent (% of total feed)				
N_2	20	2.5	2.5	10
Ar	0	17.5	0	0
CO_2	0	0	17.5	0
H_2O	0	0	0	10
Carbon atom selectivity (%)				
C_2H_4	62	61	65	63
CO	16	16	17	16
CO_2	8	9	7	8
CH_4	7	8	7	7
C_2H_2	3	4	1	3
Other	4	2	3	3
Hydrogen atom selectivity (%)				
H_2	22	22	22	23
H_2O	21	21	24	22
Conversion (%)				
C_2H_6	89	90	86	88
O_2	100	100	100	100
Temperature (°C)				
Front	848	942	594	674
Rear	900	862	850	882

Table 12. Carbon and hydrogen atom selectivity, conversion, and temperature for ethane oxidative dehydrogenation over a 1.0 wt. % Cu – 9.0 wt. % Cr_2O_3/ZrO_2 catalyst at a C_2H_6/O_2 ratio of 2.4 with 20% total dilution at a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Diluent (% of total feed)				
N_2	20	2.5	2.5	10
Ar	0	17.5	0	0
CO_2	0	0	17.5	0
H_2O	0	0	0	10
Carbon atom selectivity (%)				
C_2H_4	72	72	72	73
CO	9	10	9	8
CO_2	11	11	11	12
CH_4	4	4	3	4
C_2H_2	1	1	0	1
Other	3	2	3	3
Hydrogen atom selectivity (%)				
H_2	18	20	17	16
H_2O	25	24	27	27
Conversion (%)				
C_2H_6	64	62	57	59
O_2	100	100	100	100
Temperature (°C)				
Front	257	657	412	421
Rear	834	796	794	839

however, does change slightly with different diluents. Along with the decrease in ethane conversion, the reaction temperature at the back of the catalyst is also lower with the CO_2 and H_2O diluent. Therefore, use of diluents with different heat capacities has the effect of lowering the ethane conversion and temperature at the back of the catalyst with increases in the heat capacity of the diluent used. The use of CO_2 and H_2O which are reaction products in the oxidative dehydrogenation of ethane as the diluent does not significantly affect the product selectivities under these reaction conditions.

Example 7: Table 13 shows typical reactor performance for the oxidative dehydrogenation of propane over a variety of monolithic catalysts at nitrogen dilutions levels of 20% and 50% at total flow rate of 2 SLPM. The less expensive chromium oxide catalyst shows similar selectivity and conversion trends as the Pt catalyst with significantly less production of CO.

Table 13: Carbon atom and hydrogen atom selectivity, conversion, and temperature for propane oxidation over various catalysts at several C_3H_8/O_2 ratios with 20% and 50% N_2 dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	6 wt. % Cr_2O_3/ZrO_2							6 wt. % $Pt/\alpha-Al_2O_3$							
N_2 dilution (%)	20				50			20				50			
C_3H_8/O_2	1.2	1.5	1.8	2.0	1.2	1.5	1.8	1.2	1.5	1.8	2.0	1.2	1.5	1.8	2.0
Carbon atom selectivity (%)															
C_3H_6	1.2	10.3	20.7	26.0	1.1	11.0	22.7	2.8	16.0	23.5	27.7	1.1	15.1	22.6	26.1
C_2H_4	37.8	45.5	40.7	37.7	34.6	43.1	34.3	37.7	38.7	33.4	32.1	31.3	37.3	29.2	23.8
CO	21.0	9.1	6.3	5.3	23.3	11.0	9.2	26.6	17.0	16.5	13.9	33.6	17.8	18.5	20.7
CO_2	7.5	8.2	9.0	9.9	9.1	10.9	15.5	3.8	4.1	6.1	6.8	5.8	7.9	12.2	15.0
CH_4	23.3	19.8	16.8	15.6	21.7	17.0	13.0	22.6	18.4	15.7	15.1	20.7	16.7	13.4	11.2
C_2H_6	1.1	2.6	2.5	2.3	0.7	2.4	2.1	1.6	2.4	2.1	2.0	0.9	2.2	1.9	1.5
C_3H_2	5.9	1.5	0.8	0.5	7.4	2.0	0.5	3.1	0.8	0.1	0.1	4.5	0.5	0.2	0.1
Other	2.1	2.9	3.1	2.8	2.3	2.6	2.7	1.8	2.6	2.6	2.2	2.1	2.6	2.1	1.6
Hydrogen atom selectivity (%)															
H_2	20.1	9.5	7.4	6.5	19.4	10.0	7.9	16.4	8.2	6.9	5.6	19.9	8.6	8.2	6.8
H_2O	13.4	15.9	16.9	17.9	18.9	19.3	26.1	17.5	19.5	24.7	24.6	21.5	23.0	29.5	36.3
Conversion (%)															
C_3H_8	99.9	92.3	74.3	60.8	100	91.5	64.0	99.3	83.3	63.8	52.5	99.9	83.1	57.1	39.3
O_2	100	99.5	99.1	99.1	100	99.7	98.9	99.3	98.2	97.7	97.8	99.4	98.4	98.0	97.7
Temperature (°C)															
Front	1066	678	584	529	1027	623	500	980	622	545	505	1018	941	921	849
Rear	965	875	829	808	934	852	800	969	909	876	866	937	831	825	815

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surveying a wide variety of metal oxides for high selectivity and conversion [Carra, S. and Forni, L., *Catal. Rev.* 1971, *5*, 159-198; Cimino, A. et al, *J. Mol. Catal.* 1989, *55*, 23-33; US Patent #4535067; US Patent #4804799; US Patent #3965044; US Patent #5354935; US Patent #5254788; US Patent #5378350; US Patent #3719721; US Patent #4032589]. However, these catalysts generally deactivate with time on stream due to coke build-up on the catalyst surface [Royo, C. et al, *Ind. Eng. Chem. Res.* 1994, *33*, 2563-2570].

Catalytic oxidative dehydrogenation of hydrocarbons is an alternative to thermal pyrolysis and catalytic dehydrogenation. The oxidative dehydrogenation of C_2-C_6 hydrocarbons has been examined over noble metal catalysts supported on ceramic foam monoliths [Flick, D. W. and Huff, M. C., *Appl. Catal. A* 1999 187, 13-24; Flick, D. W. and Huff, M. C., *Abstracts of Papers of ACS* 217:O18-CATL, Part 2 March 21, 1999; Flick, D. W. and Huff, M. C., *Catal Lett* 1997, *47*, 91-97; Flick, D. W. and Huff, M. C., *J. Catal.* 1998, *178*, 315-327; Dietz III, A. G. et al, *J. Catal.* 1998, *176*, 459-473; Huff, M. C. et al, *Catal. Today* 1994, *21*, 113-128; US Patent # 5905180 which are all incorporated by reference in its entirety for all useful purposes]. In general, noble metal catalysts are more expensive than oxide catalysts. The oxidative dehydrogenation of ethane over Pt-coated monolith catalysts at short contact times has been investigated concerning the maximization of C_2H_4 production [US Patent #5382741; US Patent #5625111; Huff, M. and Schmidt, L. D., *J. Phys. Chem.* 1993, *97*, 11815-11822; US Patent #4844837; US Patent #4940826; US Patent #5105052; US Patent #5593935; Witt, P. M. and Schmidt, L. D., *J. Catal.* 1996, *163*, 465-475; US Patent # 5905180]. These monolith reactors operate at very short contact times on the order of milliseconds. The yield of C_2H_4 with these reactors has been shown to be about 50% (C_2H_4 selectivity ~65% at around 80% conversion).

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Example 8: Table 14 shows typical reactor performance for the oxidative dehydrogenation of butane over a variety of monolithic catalysts at nitrogen dilution levels of 20% at total flow rate of 2 SLPM. Again, the less expensive chromium oxide catalyst shows similar selectivity and conversion trends with changes in the fuel to oxygen ratio as the Pt catalyst. In general, the chromium oxide catalysts have a higher conversion of the hydrocarbon and selectivity to C_2H_4 than the Pt catalyst. The chromium oxide catalysts produce less CO especially at the higher fuel to oxygen ratios.

Table 14: Carbon atom and hydrogen atom selectivity, conversion, and temperature for butane oxidation over various catalysts at several C_4H_{10}/O_2 ratios with 20% dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalysts	3 wt. % Pt/Al2O3	1wt% Cu – 9 wt% Cr2O3/ZrO2	2 wt% MnOx - 1wt% Cu – 10 wt% Cr2O3/ZrO2	5 wt% MgO -1wt% Cu – 10 wt% Cr2O3/ZrO2	3 wt. % Pt/Al2O3	1wt% Cu – 9 wt% Cr2O3/ZrO2	2 wt% MnOx - 1wt% Cu – 10 wt% Cr2O3/ZrO2	5 wt% MgO -1wt% Cu – 10 wt% Cr2O3/ZrO2
C_4H_{10}/O_2 ratio			1.5				2.0	
Carbon atom selectivity (%)								
C_4H_{10}	1	0	1	1	6	5	6	4
C_3H_6	16	7	15	12	30	26	26	28
C_2H_4	39	46	39	42	20	25	24	26
CO	17	13	18	16	8	6	6	5
CO_2	4	8	6	7	19	17	20	20
CH_4	15	16	15	15	11	10	10	11
C_2H_6	3	2	3	3	3	3	3	3
C_2H_2	1	1	1	2	0	0	0	0
Other	3	7	3	3	3	8	4	4
Hydrogen atom selectivity (%)								
H_2	6	11	10	11	2	4	4	4
H_2O	14	10	12	11	23	17	22	18
Conversion (%)								
C_4H_{10}	93	99	93	95	28	37	30	33
O_2	98	100	100	99	98	100	100	100
Temperature (°C)								
Front	512	542	999	966	140	68	390	367
Rear	861	870	751	820	713	724	657	702

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Example 9: Table 15 shows typical reactor performance for the oxidative dehydrogenation of isobutane over a variety of monolithic catalysts at nitrogen dilution levels of 20% at total flow rate of 2 SLPM. Again, the less expensive chromium oxide catalyst shows similar selectivity and conversion trends with changes in the fuel to

5   oxygen ratio as the Pt catalyst. In general, the chromium oxide catalysts have a higher conversion of the hydrocarbon and selectivity to C_2H_4 than the Pt catalyst. The chromium oxide catalysts produce less CO especially at the higher fuel to oxygen ratios.

Table 15: Carbon atom and hydrogen atom selectivity, conversion, and temperature for isobutane oxidation over various catalysts at several iC_4H_{10}/O_2 ratios with 20% dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalysts	3 wt. % Pt/Al$_2$O$_3$	1wt% Cu – 9 wt% Cr$_2$O$_3$/ZrO$_2$	2 wt% Ni – 1wt% Cu – 10 wt% Cr$_2$O$_3$/ZrO$_2$	3 wt. % Pt/Al$_2$O$_3$	1wt% Cu – 9 wt% Cr$_2$O$_3$/ZrO$_2$	2 wt% Ni – 1wt% Cu – 10 wt% Cr$_2$O$_3$/ZrO$_2$
i-C$_4$H$_{10}$/O$_2$ ratio	1.5			2.0		
Carbon atom selectivity (%)						
i-C$_4$H$_{10}$	19	11	11	27	22	23
C$_4$H$_{10}$	2	2	3	1	4	2
C$_3$H$_6$	27	27	32	27	31	33
C$_2$H$_4$	6	14	13	2	5	6
CO	11	12	12	19	8	7
CO$_2$	7	8	8	11	12	12
CH$_4$	15	19	18	11	14	14
Other	14	7	3	2	4	4
Hydrogen atom selectivity (%)						
H$_2$	6	7	6	3	4	4
H$_2$O	9	7	7	5	6	6
Conversion (%)						
i-C$_4$H$_{10}$	71	87	89	44	57	58
O$_2$	98	99	99	98	99	99
Temperature (°C)						
Front	900	1033	1023	840	634	984
Rear	830	817	790	788	761	733

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In addition to Pt-coated foam monoliths, Yokoyama, et. al. [Yokoyama, C. et al, *Catal Lett* **1996**, *38*, 181-188; US Patent # 5905180] examined the addition of various metal promoters to Pt-coated foam monoliths for the autothermal oxidative dehydrogenation of ethane at millisecond contact times. Their study found that the addition of Sn and Cu to Pt-monoliths enhanced the C_2H_4 selectivity and C_2H_6 conversion with no deactivation or volatilization of the catalyst. For the Pt-Sn catalyst, the ethane conversion increased by up to 6% and the ethylene selectivity increased by up to 5%. For the Pt-Cu catalyst, the conversion and ethylene selectivity were higher than Pt alone, but showed less improvement than the Pt-Sn catalyst.

Researchers have also examined oxidative dehydrogenation over oxide catalysts [US Patent #4658074; US Patent #5430209; US Patent #5439859; US Patent #3862255; US Patent #5759946; US Patent #4026920]. These preocesses prodice olefins with yields less than 45%.

The activity and selectivity of chromium oxide-supported catalysts in alkane dehydrogenation has been known for many decades [Frey, F. E. and Huppke, W. F., *Ind. Eng. Chem.* **1933**, *25*, 54; Marcilly, C. and Delmon, B., *J. Catal.* **1972**, *24*, 336-347]. Due to their importance in hydrogenation, dehydrogenation, and polymerization reactions, chromium-containing heterogeneous catalysts have been studied by a variety of techniques by a large number of researchers in the past several decades. For the supported chromium Phillips polymerization catalyst, much of the research has focused on the structure and oxidation state of the reactive chromium surface species [Zecchina, A. et al, *J. Phys. Chem.* **1975**, *79*, 966-972; Weckhuysen, B. M. et al, *Chem. Rev.* **1996**, *96*, 3327-3349]. It is now generally accepted that the catalytic properties of the supported chromium oxide are due to the surface chromium species formed as a result of chromium-support interactions [Kim, D. S. and Wachs, I.

Example 10: The copper modified chromium oxide catalyst supported on a zirconia monolith shows excellent stability for the oxidative dehydrogenation of ethane even at high C_2H_6/O_2 ratios and high flow rates where other catalysts tend to deactivate. Typical reactor performance is shown in Table 16.

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Table 16: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi. 6.7% Cu - 6.7% Cr_2O_3/ZrO_2 monolith as a function of flow rate at several C_2H_6/O_2 ratios with 50% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm.

C_2H_6/O_2	1.5					1.8					2.4			
Flowrate (SLPM)	2	3	4	5	6	2	3	4	5	6	2	3	4	5
Carbon atom selectivity (%)														
C_2H_4	62.7	59.1	57.8	55.8	55.7	71.0	68.0	67.7	67.8	65.9	66.0	69.2	70.2	70.4
CO	13.4	13.8	14.5	15.0	15.2	7.0	8.8	8.7	8.9	11.7	5.0	5.3	5.5	5.4
CO_2	11.1	10.7	10.9	10.8	11.3	14.1	13.3	13.5	13.4	12.9	25.3	20.8	19.0	18.9
CH_4	6.6	7.3	8.0	8.4	8.3	4.2	4.8	5.0	5.0	5.5	1.9	2.4	2.7	2.7
C_2H_2	3.1	5.6	6.2	6.6	6.0	1.5	2.0	2.0	1.8	0.8	0.2	0.4	0.4	0.4
Other	3.2	3.5	2.7	3.4	3.4	2.3	3.1	3.2	3.1	3.2	1.7	2.0	2.2	2.3
Hydrogen atom selectivity (%)														
H_2	16.6	19.6	21.3	22.0	23.3	15.3	17.5	18.5	19.1	18.9	13.1	15.8	16.9	17.3
H_2O	27.8	25.2	24.0	22.9	21.2	28.6	26.3	25.5	24.6	25.3	39.8	32.4	29.3	28.8
Conversion (%)														
C_2H_6	89.2	92.3	93.4	94.4	94.5	70.5	76.8	77.5	77.8	75.5	37.3	46.2	50.1	50.5
O_2	99.9	99.9	99.8	99.8	99.7	99.9	99.8	99.7	99.6	98.8	100	99.9	99.9	99.8
Temperature (°C)														
Front	408	123	171	131	97	441	99	104	96	75	243	160	104	77
Rear	838	878	901	912	906	762	830	841	848	830	777	813	835	856

Example 11: The oxidative dehydrogenation of ethane was investigated where the feed gas to the reactor contained C_2H_6, O_2, and H_2 with a small amount of N_2 for use as an internal calibration standard. The level of H_2 in the feed ranged from 0 to 50% that corresponded to H_2/O_2 ratios ranging from 0 to 3.0. The amount of N_2 in the feed was always less than 1%. In the range of conditions studied, no flames were observed.

The addition of H_2 (Table 17) during the oxidative dehydrogenation of ethane over a 1.0% Cu – 9.0% Cr_2O_3/ZrO_2 monolith catalyst with less than 1% N_2 dilution at a total feed flow rate of 7 SLPM results in a significant increase in the C_2H_4 selectivity. At a C_2H_6/O_2 ratio of 2.0, the selectivity to C_2H_4 increases from 56% with no H_2 addition to

5   76% with a H_2/O_2 ratio of 3.0 in the reactor feed. At a C_2H_6/O_2 ratio of 2.4, the selectivity to C_2H_4 increases from 68% with no H_2 addition to 81% with a H_2/O_2 ratio of 3.0 in the reactor feed. The increase in the C_2H_4 selectivity corresponds with a decrease in the selectivity to CO and CO_2. The selectivity to CO and CO_2 falls proportionally with increasing H_2 in the feed. The selectivity to CH_4 also falls slightly with increasing H_2

10   addition. The addition of H_2, however, also results in a decrease in the C_2H_6 conversion which falls from 94% to 81% at a C_2H_6/O_2 ratio of 2.0, and 80% to 66% at a C_2H_6/O_2 ratio of 2.4 as the H_2/O_2 feed ratio increases from 0 to 3. Along with the decrease in the C_2H_6 conversion, the temperature measured at the exit of the catalyst at both C_2H_6/O_2

Table 17: Carbon and hydrogen atom selectivity, conversion, C_2H_4 yield, and temperature for ethane oxidation over a 45 ppi, 1.0% Cu – 9.0% Cr_2O_3/ZrO_2 monolith as a function of the H_2/O_2 ratio at C_2H_6/O_2 ratios of 2.0 and 2.4 at a total flow rate of 7 SLPM with less than 1% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm.

C_2H_6/O_2	2.0				2.4			
H_2/O_2	0	1	2	3	0	1	2	3
Carbon atom selectivity (%)								
C_2H_4	56	64	71	75	68	74	78	81
CO	18	14	11	9	11	9	8	6
CO_2	8	6	5	4	8	6	5	4
CH_4	9	8	8	7	6	6	5	5
C_2H_2	5	3	2	2	1	1	1	1
Other	4	4	3	3	4	4	3	3
Hydrogen atom selectivity (%)								
H_2	22	17	11	4	19	9	5	1
H_2O	31	33	35	39	31	36	37	42
Conversion (%)								
C_2H_6	94	90	86	81	80	78	71	66
O_2	100	100	100	100	100	100	100	100
Temperature (°C)								
Front	161	60	55	46	48	28	30	31
Rear	881	860	839	822	849	826	812	795
Carbon atom yield (%)								
C_2H_4	53	58	60	61	55	58	55	54

ratios falls with increasing H_2 content in the feed. Thus, the overall production or yield of C_2H_4 in the reaction system is also affected by H_2 addition in the feed since the selectivity to C_2H_4 increases with H_2 addition and the C_2H_6 conversion decreases with the addition of H_2. At a C_2H_6/O_2 ratio of 2.0, the C_2H_4 yield steadily increases with

5   higher H_2/O_2 ratios in the feed, but the marginal increase decreases at the higher H_2/O_2 ratios. Thus, the selectivity to the desired product, C_2H_4, increases faster than the decrease in the C_2H_6 conversion with increasing H_2 concentration in the feed. At a C_2H_6/O_2 ratio of 2.4, the yield of C_2H_4 goes through a maximum at a H_2/O_2 of 1.0. This directly results from the fact that at a H_2/O_2 below 1, the C_2H_4 selectivity rises faster than the corresponding decrease in C_2H_6 conversion. However, at a H_2/O_2 ratio of 2 or

10   above, the C_2H_4 selectivity rises slower than the decrease in the conversion of C_2H_6.

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Table 1: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various catalysts at several C_2H_6/O_2 ratios with 20% N_2 dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	10 wt. % Cr_2O_3/α-Al_2O_3			Pt-10 wt. % Cr_2O_3/α-Al_2O_3			9 wt. % Cr_2O_3/ZrO_2					6.7 wt. % Cu & 6.7 wt. % Cr/ZrO_2					3 wt. % Pt/α-Al_2O_3				
C_2H_6/O_2	1.2	1.5	1.8	1.2	1.5	1.8	1.2	1.5	1.8	2.2	2.4	1.2	1.5	1.8	2.2	2.4	1.2	1.5	1.8	2.2	2.4
Carbon atom selectivity (%)																					
C_2H_4	19	44	56	20	45	62	32	55	67	70	70	14	43	62	72	73	31	57	65	64	62
CO	42	30	25	41	30	19	36	18	11	9	9	50	32	17	8	7	40	26	17	16	15
CO_2	7	7	6	4	5	8	8	10	12	14	17	4	5	8	11	13	3	3	6	11	14
CH_4	14	11	9	14	11	7	13	8	5	3	2	13	10	7	5	4	13	8	6	4	4
C_2H_2	16	3	0.3	15	6	1	11	4	1	1	0.3	15	10	5	1	1	10	2	0.4	0.1	0
other	2	5	4	7	4	4	0.3	4	4	3	3	3	0	0	2	3	4	4	7	5	6
Hydrogen atom selectivity (%)																					
H_2	56	44	37	58	43	34	47	32	27	25	24	45	32	24	19	18	39	27	22	16	14
H_2O	16	17	19	15	17	19	20	24	25	27	30	19	20	21	22	23	24	25	29	36	40
Conversion (%)																					
C_2H_6	100	97	81	100	95	82	100	98	90	72	64	100	97	87	72	63	100	95	80	65	57
O_2	100	100	99	100	100	100	100	100	100	100	100	100	100	100	98	99	100	100	100	100	99
Temperature (°C)																					
Front	1183	675	228	1249	205	167	1164	1000	830	675	620	1132	1025	1020	380	346	1162	710	512	396	365
Rear	978	898	570	1003	947	992	875	816	775	753	745	892	825	792	768	757	1013	923	885	866	853

EXAMPLES

Example 1: The oxidative dehydrogenation of ethane was examined over a variety of catalysts supported on ceramic foam monoliths at a flowrate of 2 standard liters per minute (SLPM) which corresponds to a contact time of approximately 15 ms (GHSV = 200,000 hr^{-1}). The ceramic foam monolith supports (alpha-alumina or magnesia stabalized zirconia were obtained from Vesuvius Hi-Tech Ceramics and contain 45 ppi (pores per linear inch). Chromium was deposited on the support surface by exposing the ceramic to a liquid solution containing chromium ions such as aqueous chromium nitrate. Platinum was deposited on the support surface by exposing the ceramic to a liquid solution containing platinum ions such as aqueous chloroplatinic acid. Copper was deposited on the support surface by exposing the ceramic to a liquid solution containing copper ions such as aqueous copper nitrate. Between depositions, the catalysts were calcined in air.

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Table 1 shows product carbon and hydrogen atom selectivity, conversion, and reaction temperature at several C_2H_6/O_2 ratios in the feed gas with 20% N_2 dilution for 10 wt. % Cr_2O_3/α-Al_2O_3, 9 wt. % Cr_2O_3/ZrO_2, 3 wt. % Pt/α-Al_2O_3, 6.7 wt. % Cu - 6.7 wt. % Cr/ZrO_2 and Pt (0.05 wt. %) modified 10 wt. % Cr_2O_3/α-Al_2O_3 catalysts. At a C_2H_6/O_2 ratio of 1.2, the 9 wt. % Cr_2O_3/Al_2O_3 and Pt modified 10 wt. % Cr_2O_3/Al_2O_3 catalysts have a C_2H_4 selectivity around 20% compared to the 30% and 32% selectivity to C_2H_4 seen for the 3 wt. % Pt/α-Al_2O_3 and 9 wt. % Cr_2O_3/ZrO_2 catalysts respectively. The CO selectivity is approximately 40% for all the catalysts except for the Cr_2O_3/ZrO_2 catalyst which showed a slightly lower selectivity to CO of approximately 35% and the Cu modified catalyst which showed a slightly higher selectivity to CO of ~50%. For the selectivity to CO_2, a significant difference can be seen between the Cr_2O_3 and Pt catalysts with more CO_2 formed over the Cr_2O_3 than over Pt. The CO_2 selectivity for the Pt-modified chromium oxide catalyst falls directly between the two single component catalysts. The CH_4 selectivity, however, is essentially the same for all the catalysts at approximately 13%. The selectivity to C_2H_2 is slightly higher for the Cr_2O_3/Al_2O_3 and the Cu modified catalyst than the three other catalysts. At a C_2H_6/O_2 ratio of 1.2, the highest selectivity to H_2 is about 56% for the Cr_2O_3/Al_2O_3 and Pt-modified Cr_2O_3/Al_2O_3 catalysts. The H_2 selectivity for the Cr_2O_3/ZrO_2 was 47% and the Pt/Al_2O_3 catalyst was 39%. The corresponding selectivity to H_2O is higher for the Pt/Al_2O_3 and Cr_2O_3/ZrO_2 catalysts than the two Cr_2O_3/Al_2O_3 catalysts.

Similar trends between the catalysts exist at higher C_2H_6/O_2 ratios. The Cr_2O_3/ZrO_2 catalyst and the Cu modified Cr_2O_3/ZrO_2 catalyst show the best C_2H_4 selectivity at the highest C_2H_6/O_2 ratios with the Cu modified Cr_2O_3/ZrO_2 catalyst showing the lowest selectivity to CO. The C_2H_6 conversion and C_2H_4 yield is higher over the Cr_2O_3/ZrO_2 catalyst and the Cu modified Cr_2O_3/ZrO_2 catalyst than over the Pt

catalyst; the difference increases with increasing ratios of C_2H_6/O_2 in the feed. At C_2H_6/O_2 ratios of 1.2 and 1.5, the C_2H_4 selectivity for the Cr_2O_3/ZrO_2 and the Pt/Al_2O_3 catalysts is essentially the same with a lower C_2H_4 selectivity for the Cu modified Cr_2O_3/ZrO_2 catalyst. But at the higher C_2H_6/O_2 ratios, the selectivity to C_2H_4 is higher over the chromium oxide and Cu modified chromium oxide catalysts at >70% compared to <65% over the Pt catalyst. The H_2 selectivity for the Cr_2O_3/ZrO_2 catalyst and the Cu modified Cr_2O_3/ZrO_2 catalyst is also higher at all C_2H_6/O_2 ratios, especially at the higher C_2H_6/O_2 ratios. The CO selectivity is lower for the chromium oxide-zirconia catalyst and at the higher C_2H_6/O_2 ratios is approximately half of the CO selectivity for the Pt catalyst. This reduction in CO production is even more evident at the higher C_2H_6/O_2 ratios over the Cu modified Cr_2O_3/ZrO_2 catalyst. However, the selectivity towards complete combustion products, CO_2 and H_2O, is higher over the Cr_2O_3/ZrO_2.

All catalysts exhibit similar C_2H_6 conversions with lower conversions at the higher C_2H_6/O_2 ratios. At C_2H_6/O_2 ratios greater than 1.2, the chromium oxide containing catalysts all show a slightly higher C_2H_6 conversion than the Pt monolith. In all cases, O_2 is essentially completely consumed.

Example 2: The oxidative dehydrogenation of ethane was examined over a large variety of catalysts supported on ceramic foam monoliths at flow rates ranging from 2 to 4 standard liters per minute (SLPM) which corresponds roughly to catalyst contact times of 5-15 ms (GHSV = 80,000 – 200,000 hr^{-1}).

Table 2 shows product carbon and hydrogen atom selectivity, conversion, and reaction temperature at a C_2H_6/O_2 ratio of 2.0 in the feed gas with 20% N_2 dilution at a total feed flow rate of 2.0 SLPM for the oxidative dehydrogenation of ethane over single component catalysts. The Cr_2O_3, CuO, and MnO_x catalysts on a ZrO_2 monolith have

Table 2: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various single component catalysts at a C_2H_6/O_2 ratio of 2.0 with 20% N_2 dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	3 wt. % Pt/Al$_2$O$_3$	9 wt. % Cr$_2$O$_3$/ZrO$_2$	11.2 wt. % CuO/ZrO$_2$	9.7 wt. % Ni/ZrO$_2$	9.1 wt. % FeO$_x$/ZrO$_2$	8.1 wt. % MnO$_x$/ZrO$_2$
Carbon Atom Selectivity (%)						
C$_2$H$_4$	63	68	68	2	51	68
CO	22	10	10	89	31	7
CO$_2$	6	13	10	8	10	11
CH$_4$	5	4	7	0.5	6	7
C$_2$H$_2$	1	1	2	0	0	3
Other	3	3	3	0	2	4
Hydrogen Atom Selectivity (%)						
H$_2$	22	26	17	91	43	19
H$_2$O	25	26	22	6	13	22
Conversion (%)						
C$_2$H$_6$	71	81	82	45	74	83
O$_2$	100	100	100	100	100	100
Temperature (C)						
Front	939	745	392	73	268	985
Rear	836	763	807	749	745	822

essentially the same reaction results under these conditions with a C_2H_4 selectivity of ~68% with over 81% conversion of the ethane feed. These catalysts, Cr_2O_3, CuO, and MnO_x, also have very low selectivity to CO of 10%, 10%, and 7%, respectively; along with a corresponding higher CO_2 selectivity than the other single component catalysts. The 3 wt. % Pt/α-Al$_2$O$_3$ catalyst had a slightly lower selectivity to C_2H_4 and lower conversion of C_2H_6 than the Cr_2O_3, CuO, and MnO_x catalysts. Additionally, the Pt/Al$_2$O$_3$ catalyst also had a higher selectivity to CO and lower selectivity to CO_2 than the three transition metal oxide catalysts. The 9.1 wt. % FeO$_x$/ZrO$_2$ catalyst also had a lower selectivity to C_2H_4 (51%) and lower C_2H_6 conversion (74%) along with a significantly higher selectivity to CO (31%) than the Cr_2O_3, CuO, and MnO_x catalysts. In contrast to all the other single component catalysts, the 9.7 wt. % Ni on a ZrO$_2$ monolith produced primarily syngas products, CO and H_2, and not oxidative dehydrogenation products, C_2H_4 and H_2O.

Example 3: Table 3 shows the results for the oxidative dehydrogenation of ethane over Cr_2O_3/ZrO_2 monolith catalyst with the addition of a single promoter including Ag, Cu, FeO_x, Ni, MnO_x, and MgO. The reaction results for a C_2H_6/O_2 ratio of 2.0 with 20% N_2 dilution at a total flow rate of 2 SLPM show that the addition of the promoters to the Cr_2O_3/ZrO_2 catalyst can change the product selectivities and conversion over the catalyst. The addition of Cu or Ag to the Cr_2O_3/ZrO_2 catalyst does not significantly affect the product selectivities or reactant conversions. The addition of FeO_x or MgO to the Cr_2O_3/ZrO_2 catalyst results in a slight decrease in the ethane conversion from 81% to 75% and 78%, respectively, but does not significantly affect the product selectivities. In contrast, the addition of MnO_x to the Cr_2O_3/ZrO_2 catalyst results in a decrease in the C_2H_4 selectivity to 61% from 68% and a corresponding increase in the CO selectivity to 22% from 13%. The ethane conversion of the 0.8 wt. % MnO_x – 8.0 wt. % Cr_2O_3/ZrO_2 catalyst, however, is the same as the 9.0 wt. % Cr_2O_3/ZrO_2.

Table 3: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various catalysts at a C_2H_6/O_2 ratio of 2.0 with 20% N_2 dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	1.3 wt. % Cu – 13.0 wt. % Cr_2O_3/ZrO_2	2.2 wt. % Ag – 11.0 wt. % Cr_2O_3/ZrO_2	0.7 wt. % FeO_x – 7.0 wt. % Cr_2O_3/ZrO_2	0.7 wt. % Ni – 7.0 wt. % Cr_2O_3/ZrO_2	0.8 wt. % MnO_x – 8.0 wt. % Cr_2O_3/ZrO_2	0.7 wt. % MgO – 7.0 wt. % Cr_2O_3/ZrO_2
Carbon Atom Selectivity (%)						
C_2H_4	68.	68	69	46	61	68
CO	13	12	11	41	22	13
CO_2	9	10	10	9	6	10
CH_4	6	6	5	3	6	5
C_2H_2	2	2	0	0	1	1
other	3	3	4	1	3	3
Hydrogen Atom Selectivity (%)						
H_2	20	22	20	45	25	20
H_2O	22	22	24	20	23	23
Conversion (%)						
C_2H_6	80	80	75	60	81	78
O_2	100	100	100	100	100	100
Temperature (C)						
Front	545	939	1044	988	999	934
Rear	856	836	833	798	821	796

Example 4: Table 4 shows the results for multi-component catalysts for the oxidative dehydrogenation of ethane for a C_2H_6/O_2 ratio of 2.0 with 20% N_2 dilution at a total flow rate of 2 SLPM. The addition of MgO, FeO_x, and MnO_x to a $Cu/Cr_2O_3/ZrO_2$ results in a lower selectivity to C_2H_4 and corresponding higher selectivity to CO along with a lower C_2H_6 conversion than the 1.3 wt. % Cu – 13.0 wt. % Cr_2O_3 on a ZrO_2 monolith. The addition of Ni to the $Cu/Cr_2O_3/ZrO_2$ catalyst also resulted in a slightly lower C_2H_4 selectivity, but the addition of Ni did not significantly affect the C_2H_6 conversion.

The addition of the Cu to the Cr_2O_3/ZrO_2 catalyst does not significantly affect the product selectivity or reactant conversions as noted above. The addition of Cu, however, did significantly increase the activity of the $CuO/Cr_2O_3/ZrO_2$ catalyst especially at higher flow rates, N_2 dilutions, and C_2H_6/O_2 ratios. The 1.3 wt. % Cu – 13.0 wt. %

Table 4: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various catalysts at a C_2H_6/O_2 ratio of 2.0 with 20% N_2 dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	1.1 wt. % Cu – 11.0 wt. % MnO_x/ZrO_2	5.3 wt. % MgO – 0.9 wt. % Cu – 8.9 wt. % Cr_2O_3/ZrO_2	1.9 wt. % Ni – 0.9 wt. % Cu – 9.3 wt. % Cr_2O_3/ZrO_2	2.1 wt. % FeO_x – 1.0 wt. % Cu – 10.3 wt. % Cr_2O_3/ZrO_2	1.7 wt. % MnO_x – 0.8 wt. % Cu – 8.6 wt. % Cr_2O_3/ZrO_2
Carbon Atom Selectivity (%)					
C_2H_4	67	63	65	65	63
CO	8	22	13	19	22
CO_2	11	6	9	7	7
CH_4	6	5	6	5	5
C_2H_2	3	1	1	1	1
other	4	3	6	3	3
Hydrogen Atom Selectivity (%)					
H_2	19	23	23	24	23
H_2O	22	24	21	23	24
Conversion (%)					
C_2H_6	72	72	81	76	72
O_2	100	100	100	100	100
Temperature (C)					
Front	849	934	988	999	934
Rear	856	796	798	821	796

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Cr_2O_3/ZrO_2 catalyst was able to achieve stable operation at a C_2H_6/O_2 ratio of 2.4 with 50% N_2 dilution at a total flow rate of 10 SLPM with no signs of deactivation. In contrast, the 9 wt. % Cr_2O_3/ZrO_2 catalyst was only able to achieve stable, non-deactivating behavior at a C_2H_6/O_2 ratio of 2.4 with 50% N_2 dilution at a total flow rate of less than 4 SLPM. It was also found that the addition of the Cu promoter to a MnO_x/ZrO_2 catalyst did not result in the same dramatic increase in catalyst activity.

Example 5: Under some conditions, reaction is not sustained indefinitely over some of the supported chromium oxide catalysts. The onset of extinction depends on the composition of the catalyst, the C_2H_6/O_2 ratio, the support material, the weight loading of the catalyst, the flowrate, the N_2 dilution, and the preheat of the feed.

The time to extinction is shown in Table 5 as a function of C_2H_6/O_2 ratio with 20% reactant dilution at a flowrate of 2 SLPM for the various catalysts. The sustained activity of the Cr_2O_3/Al_2O_3 and the Pt/Al_2O_3 and Cr_2O_3/ZrO_2 catalysts differ in that the Pt/Al_2O_3, Cu modified Cr_2O_3/ZrO_2, and the 9 wt. % Cr_2O_3/ZrO_2 catalyst sustain reaction for a much longer period of time than the other catalyst compositions examined. Like the Pt monolith, the 10 wt. % Cr_2O_3/Al_2O_3 catalyst at a C_2H_6/O_2 ratio of 1.2 with 20% N_2 at a flowrate of 2 SLPM has shown sustained reaction for very long periods of time with no deactivation and product selectivity changes. However, at a C_2H_6/O_2 ratio of 1.5, the reaction is sustained for only 1.6 hours. Before extinction of the reaction, the product selectivity and reactant conversions are constant over the entire time period. The catalyst temperature falls slightly in the first 1.25 hours and then rapidly decreases until the reaction extinguishes. At a C_2H_6/O_2 ratio of 1.8 with 20% N_2 dilution at 2 SLPM, the reaction over the Cr_2O_3/Al_2O_3 monolith extinguishes after only 5-10 minutes.

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Table 5: The reactive lifetime of the various catalysts as a function of C_2H_6/O_2 ratio in the feed with 20% N_2 dilution with a total feed flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Fuel/O_2	1.2	1.5	1.8	2.0	2.2	2.4
Catalyst	Lifetime (hrs)					
3 % Pt/α -Al_2O_3	> 5.0*	> 5.0*	> 5.0*	> 5.0*	> 5.0*	> 5.0*
9% Cr_2O_3/ZrO_2	> 2.0*	> 2.0*	> 6.0*	> 2.0*	> 2.0*	> 2.0*
2% Cr_2O_3/ZrO_2	> 2.0*	> 2.0*	0.1	---	---	---
10% Cr_2O_3/α-Al_2O_3	> 4.0*	1.6	0.1	---	---	---
1.5% Cr_2O_3/α -Al_2O_3	0.1	< 0.1	---	---	---	---
6.7% Cu - 6.7% Cr_2O_3/ZrO_2	> 2.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 2.0*
10% Cr_2O_3/α -Al_2O_3 Pellets	> 1.0*	> 7.5*	0.2	0.2	---	---
1.3 % Cu – 13.0% Cr_2O_3/ZrO_2	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 5.0*
9.1 % FeO_x/ZrO_2	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
8.1 % MnO_x/ZrO_2	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
9.7 % Ni/ZrO_2	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
11.2 % CuO/ZrO_2	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
Pt-10% Cr_2O_3/α -Al_2O_3	> 1.0*	> 7.0*	9.0	---	---	---

* Catalyst did not show any signs of deactivation

In contrast to the Cr_2O_3/Al_2O_3 catalyst, the reaction was sustained under these conditions for the 9 wt. % Cr_2O_3/ZrO_2 catalyst and the Cu modified Cr_2O_3/ZrO_2 catalyst for longer periods, similar to the Pt/Al_2O_3 monolith catalyst. Like the Pt catalyst, a 9 wt. % Cr_2O_3/ZrO_2 catalyst showed non-deactivating steady state behavior up to a C_2H_6/O_2 ratio of 2.4 with 20% N_2 dilution at a total flowrate of 2 SLPM which is well outside of the flammability range for this system. At a C_2H_6/O_2 ratio of 1.8 with 20% N_2 dilution at 2 SLPM, the 9 wt. % Cr_2O_3/ZrO_2 monolith catalyst did not show any deactivation after 5 hours of continuous operation, while the reaction quickly extinguished under these condition for lower chromium oxide loadings on ZrO_2 and on all Cr_2O_3/Al_2O_3 catalysts. At a C_2H_6/O_2 ratio of 1.5 with 50% N_2 dilution at 2 SLPM, the Cu modified Cr_2O_3/ZrO_2 monolith catalyst did not show any deactivation for over 7 hours of continuous operation. The chromium oxide loading of the monoliths can significantly affect the catalysts. For chromium oxide supported on ZrO_2 and Al_2O_3, the activity of the catalyst increases with the chromium oxide loading.

The other transition metal oxide catalysts (11.2 wt. % Cu/ZrO_2, 9.7 wt. %

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Ni/ZrO$_2$, 9.1 wt. % FeO$_x$/ZrO$_2$, and 8.1 wt. % MnO$_x$/ZrO$_2$) are able to sustain reaction for more than one hour under these conditions. Additionally, the addition of the promoters (Ag, Ni, Mn, Mg, Fe, Cu, their oxides, and combinations thereof) to the Cr$_2$O$_3$/ZrO$_2$ led to stable operation for several hours with no signs of deactivation at a C$_2$H$_6$/O$_2$ ratio of 2.4 with 20% N$_2$ dilution at a total flow rate of 2 SLPM.

The addition of very small amounts of Pt (> 0.001g , ~0.05 wt. %), as a co-catalyst, was examined for its influence on the ability of the supported chromium oxide catalysts to sustain reaction for extended periods. Table 5 shows the time to extinction for Pt-modified Cr$_2$O$_3$/Al$_2$O$_3$ and unmodified Cr$_2$O$_3$/Al$_2$O$_3$ monolith catalysts at several C$_2$H$_6$/O$_2$ ratios with 20% N$_2$ dilution at a flowrate of 2 SLPM. The activity of Pt-coated monoliths for the oxidative dehydrogenation is relatively independent of the Pt loading, even for very small amounts of Pt [Haubein, N., *Effects of Support Material and Pt Loading on the Catalytic Oxidative Dehydrogenation of Ethane*; University of Delaware, 1997]. The addition of Pt significantly increases the length of time that reaction can be sustained over the Cr$_2$O$_3$/Al$_2$O$_3$ catalyst. However, the Pt-modified Cr$_2$O$_3$/Al$_2$O$_3$ catalyst still extinguished rapidly at the higher C$_2$H$_6$/O$_2$ ratios unlike the Pt/Al$_2$O$_3$ catalyst.

The surface area can also influence the temporal behavior of the catalyst. The surface area of the monolith supports is approximately 200 cm^2 per gram, which is approximately 400 cm^2 of total surface area for the monoliths used here. The total surface area can be increased by replacing the monolith with a packed bed of 3 mm Al$_2$O$_3$ pellets. The surface area of blank α-Al$_2$O$_3$ pellets is 9 m^2 per gram which results in a catalyst bed with approximately 27 m^2 of total surface area. The packed bed contained 60 Cr$_2$O$_3$/Al$_2$O$_3$ pellets, which was approximately equal in total weight to the chromium oxide monolith catalyst and resulted in an approximate bed depth of 1.5 cm.

Table 6: The reactive lifetime of the various catalysts as a function of the total feed flow rate at several C_2H_6/O_2 ratios in the feed with 20% N_2 dilution in an autothermal reactor at a pressure of 1.2 atm.

Fuel/O_2	1.2	1.2	1.2	1.5	1.5	1.5	1.8	1.8	1.8
Flowrate (SLPM)	1.0	2.0	3.0	1.0	2.0	3.0	1.0	2.0	3.0
Catalyst	Lifetime (hrs)								
3 % Pt/α-Al_2O_3	>2.0*	>5.0*	>2.0*	>2.0*	>5.0*	>2.0*	>2.0*	>5.0*	>2.0*
10% Cr_2O_3/α-Al_2O_3	>1.0*	>4.0*	<0.2	7.0	1.6	<0.1	?	0.1	—
1.5% Cr_2O_3/α-Al_2O_3	>6.5	0.1	---	0.1	<0.1	---	---	---	—
6.7% Cu - 6.7% Cr_2O_3/ZrO_2	?	*	*	?	*	*	?	*	*
9% Cr_2O_3/ZrO_2	>2.0*	>2.0*	>6.0*	>3.0*	>2.0*	>3.0*	>1.0*	>6.0*	2.8
4% Cr_2O_3/ZrO_2	>2.0*	>2.0*	>5.0*	>2.0*	>9.0*	1.5	?	?	?
2% Cr_2O_3/ZrO_2	*	>2.0*	?	?	?	?	?	0.1	—

* Catalyst did not show any signs of deactivation

Reaction was sustained over the 10 wt. % Cr_2O_3/α-Al_2O_3 pellets for more than about 7.5 hours with no sign of deactivation or changes in the product selectivity at a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution at a flowrate of 2 SLPM. Under the same conditions, the 10 wt. % Cr_2O_3/Al_2O_3 monolith extinguished in 1.6 hours. In addition to the difference in reactive lifetimes, the chromium oxide pellet catalyst displayed a slightly higher selectivity to C_2H_4 and lower selectivity to CO. The chromium oxide pellets also displayed a slightly lower C_2H_6 conversion, 94%, compared to 96% C_2H_6 conversion over the chromium oxide monolith. Therefore, in addition to the composition of the ceramic support, the total surface area of the catalyst can also have a significant impact upon the behavior of the supported chromium oxide catalyst.

The feed flowrate strongly affects the sustainability of reaction over the chromium oxide catalysts as shown in Table 6. For the 10 wt. % Cr_2O_3/Al_2O_3 catalyst at a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution, the reaction was sustained for 7 hours at 1 SLPM, 1.6 hours at 2 SLPM, and only a couple of minutes at a flowrate of 3 SLPM. When the chromium oxide loading is reduced, the activity of the catalyst decreases accordingly. For a 1.5 wt. % Cr_2O_3/α-Al_2O_3 monolith, reaction at 2 SLPM with 20% N_2 dilution could not be sustained even at a C_2H_6/O_2 ratio of 1.2. The total flowrate had to

be reduced by 50% to 1 SLPM before reaction over the low chromium oxide containing catalyst was sustained for an extended period of time (>6 hrs.) In spite of the lower flowrate and hence longer contact time, the catalyst did not achieve steady state. Throughout the time survey, the catalyst showed signs of deactivation with the conversion of C_2H_6 and O_2 falling with time on stream.

For the Cr_2O_3/ZrO_2 catalysts, the flowrate also strongly affects the catalyst's lifetime. At a C_2H_6/O_2 ratio of 1.5 with 20% N_2 dilution over the 4 wt. % Cr_2O_3/ZrO_2 monolith catalyst, the reaction was only sustained for 1.5 hours at a flowrate of 3 SLPM, compared to over 9 hours at 2 SLPM. Similar decreases in the lifetime with increasing flowrate, and correspondingly shorter contact time, can be seen for the 9 wt. % Cr_2O_3/ZrO_2 catalyst at the higher C_2H_6/O_2 ratios. The Cu modified Cr_2O_3/ZrO_2 catalyst showed no signs of deactivation for C_2H_6/O_2 ratios up to 2.4 and total flow rates up to 4 SLPM.

In addition to the lifetime of the catalyst, the flowrate affects the product selectivity and ethane conversion shown in Tables 7 and 8. As the flowrate increases, the selectivity to C_2H_4 decreases and the selectivity to C_2H_2 increases; the H_2O selectivity decreases; and the conversion increases slightly. The most significant effect of increasing the flowrate can be observed by examining the temperatures measured at the front and back of the catalyst. At the lowest flow rates, the temperature on the front face of the catalyst exceeds the temperature at the rear face of the catalyst; while at the higher flow rates, the front temperature is much less than the rear temperature.

The lifetime of the chromium oxide catalysts is also influenced by the N_2 dilution in the feed mixture. At 50% N_2 dilution at 2 SLPM with a C_2H_6/O_2 ratio of 1.2, the reaction over the 10 wt. % $Cr_2O_3/\alpha-Al_2O_3$ catalyst was only sustained for 20 minutes before the reaction rapidly extinguished, and at a C_2H_6/O_2 ratio of 1.5, the reaction

We claim:

1. A process to produce olefins which comprises reacting hydrocarbons and an oxygen containing gas in the presence of a catalyst comprising a chromium containing compound, a copper containing compound, a manganese containing compound, or combinations thereof supported on a monolith.

2. A process as claimed in claim 1 wherein said reacting hydrocarbons comprise at least one saturated hydrocarbon containing 2 to 6 carbon atoms.

3. A process as claimed in claim 1 wherein oxygen gas comprises 5 to 40% (by volume) of the reacting feed.

4. A process as claimed in claim 1, wherein the catalyst contact time is less than 0.02 seconds.

5. The process as claimed in claim 1, wherein said chromium containing compound is a chromium oxide stable at temperature in excess of about 900° C.

6. The process as claimed in claim 1, wherein said monolith is ceramic and has a honeycomb or foam structure.

7. The process as claimed in claim 1, wherein said monolith is composed of Al_2O_3, SiO_2, Mg-stabilized ZrO_2, Y-stabilized ZrO_2, or mixtures thereof.

8. The process as claimed in claim 1, wherein said monolith is composed of Mg-stabilized ZrO_2.

9. The process as claimed in claim 6, wherein said monolith has a foam structure and has about 20 to about 100 pores per linear inch.

10. The process as claimed in claim 6, wherein said catalyst contains substantially no platinum.

11. The process as claimed in claim 1, wherein said monolith further comprises

at least one promoter selected from the group consisting of Mn, Mg, Ni, Fe, Ag, Pt, and oxides thereof.

12. The process as claimed in claim 1, wherein said catalyst is present in the substantial absence of platinum.

13. The process as claimed in claim 1, wherein the ratio of atoms of Cu to Cr is between about 1:100 and about 1:2.

14. The process as claimed in claim 1, wherein the ratio of atoms of Cu to Cr is between 1:15 and 1:5.

15. The process as claimed in claim 4 wherein the reacting hydrocarbons and oxygen containing gas contains at least one hydrocarbon at ambient temperature.

16. The process as claimed in claim 4 wherein the reacting hydrocarbons and oxygen containing gas contains at least one hydrocarbon at a temperature below about 400°C.

17. The process as claimed in claim 1 wherein the oxygen containing gas comprises at least one of N_2, Ar, He, CO_2, and H_2O.

18. The process as claimed in claim 1 wherein the oxygen containing gas also contains H_2.

19. A catalyst which comprises a monolith impregnated with a Cr containing compound.

20. The catalyst as claimed in claim 19, wherein said monolith is ceramic and has a honeycomb or foam structure.

21. The catalyst as claimed in claim 19, wherein the monolith is a ceramic foam and contains about 20 to about 100 pores per linear inch.

22. The catalyst as claimed in claim 19, wherein said Cr containing compound is

Cr oxide.

23. The catalyst as claimed in claim 22, wherein said monolith is composed of Al_2O_3, SiO_2, Mg-stabilized ZrO_2 or Y-stabilized ZrO_2.

24. The catalyst as claimed in claim 19, wherein said monolith is composed of Mg-stabalized ZrO_2.

25. The catalyst as claimed in claim 19, wherein copper or copper oxide is present.

26. The catalyst as claimed in claim 25, wherein the ratio of atoms of Cu to Cr is between about 1:100 and about 1:2.

27. The catalyst as claimed in claim 25, wherein the ratio of atoms of Cu to Cr is between 1:15 and 1:5.

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :Please See Extra Sheet.
US CL :585/654, 658; 502/305, 308, 317, 318, 319, 320, 324, 345, 346

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/654, 658; 502/305, 308, 317, 318, 319, 320, 324, 345, 346

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST
search terms: oxidative dehydrogenation, copper, manganese, chromium, foam

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 4,751,336 A (JEZL et al) 14 June 1988 (14/06/88), see column 5, lines 35-65, column 7, lines 36-44, column 8, lines 4-20 and 21-30, column 28, lines 35-37 and column 4, lines 45-48.	1-5, 7, 11-19, 22, 23, 25-27 --------------- 6, 8-10, 20, 21, 24
Y,P	US 5,905,180 A (YOKOYAMA et al) 18 May 1999 (18/05/99), see abstract, lines 1-3, column 1, lines 64-67 and column 3, lines 1-60.	6, 9, 10, 21
X ---- Y	US 4,810,685 A (TWIGG et al) 07 March 1989 (07/03/89), see column 2, lines 62-68, column 4, lines 40-45, column 5, lines 60-61 and column 8, lines 3-14.	19, 20, 22, 23, 25-27 --------------- 21, 24

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search	Date of mailing of the international search report
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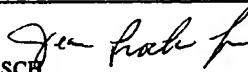
Form PCT/ISA/210 (second sheet) (July 1998)*

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,162,234 A (GRASSELLI et al) 24 July 1979 (24/07/79), See entire document.	1-27
A	US 4,711,870 A (YAMADA et al) 08 December 1987, see column 4, lines 22-24 and 41-53 and column 5, lines 8-10.	19-27
A	US 5,439,859 A (DURANTE et al) 08 August 1995 (08/08/95), see entire document.	1-27
A	US 5,306,411 A (MAZANEC et al) 26 April 1994 (26/04/94), see entire document.	1-27
A	US 5,591,315 A (MAZANCE et al) 07 January 1997 (07/01/97), see entire document.	1-27
Y	US 5,137,862 A (MACKRODT et al) 11 August 1992 (11/08/92), see column 3, lines 67-68 and column 4, lines 1-8.	8, 24

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (7):

C07C 5/327, 5/333; B01J 23/16, 23/24, 23/26, 23/32, 23/34, 23/72